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EXCHANGE NARROWINC OF DPPH LINE SHAPE IN ESR

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The line width of Paramagnetic resonance lines in solids and liquids is mostly controlled by : (i) dipole-diple interaction, (ii) spin-lattice interaction and (iii) exchange interaction.

Van-Vleck (1948) discussedthe broadening, taking in view the effect of dipole-dipole interactions and suggested that in the absence of exchange interaction which is true for dilute paramagnetic salts, the Gaussian function becomes a fair approximation to the line shape. The theory of VanVleck could not estimate the line width in substances showing large exchange phenomenon when the curve falls off rapidly. Anderson and Weiss (1953) discussed the line shape in paramagnetic resonance where large exchange interaction is present. Their theory showed Lotentzian line shape which have been verified experimentally by many workers for certain substances. Kubo and Tomita (1954) discussed the theory of Magnetic resonance on quantum mechanical basis and expressed that in presence of large exchange interaction the line shape is Lorentzian and the expression for half width between half maximum absorption points can be represented as.

$$\Delta\omega = \frac{4.18\omega^2_{10}}{\omega_{20}} \quad \ldots \quad (1)$$

where

ω^2_{10} is the width due to *dd* interactions and ω_{20} is the narrowing due to exchange.

The expressions for ω^2_{10} and ω_{20} have been given by Chirkov and Kokin (1958), are as follows,

$$\omega^2_{10} = 3.79 g^4 \beta^4 \hbar^{-2} d^{-6} \quad (2)$$

and

$$\omega_{20} = 3.65\,|J|\,h \quad \ldots \quad (3)$$

wheo.

d is mean spin distance,

and *J* is exchange integral,

Substituting the values of, $g = 2.0036$, Holden, Yager and Merritt (1951), β and $\hbar$ in the expressions 2 and 3, it is found that,

$$\omega^2_{10} = 40.62X\ d^{-6} X 10^{-26}\ \text{sec}^{-2}. \quad \ldots \quad (4)$$

and

$$\omega_{20} = 3.462 \times 10^{34} \times |J|\ \text{sec.}^{-1} \quad \ldots \quad (5)$$

In the present paper the value of the exchange integral J for different mean spin distances for DPPH has been calculated with the help of expressions 1,4 and 5, using the measured values of $\Delta\omega$, Bruin and Bruin (1956) with varying mean spin distance from 9Å to 14.5Å and within the temperature range of 100°K to 400°K in powder DPPH. The values of ω^2_{10} have been computed and taking these computed values of ω^2_{10} and measured values of $\Delta\omega$ for different mean spin distances d and the temperatures, the values of ω_{20}, the width, due to narrowing have been calculated. These values of ω_{20} have been used for obtaining the different values of J.

RESULT

The value of the exchange integral J as found above lies between 5.57×10^{-24} Joules and 0.07×10^{-24} Joules for mean spin distances varying from 9Å to 14.5Å. In the case of powder DPPH with mean spin distance of 9Å, and between the temperature range of 100°K to 400K, the value lies between 3.32×10^{-24} Joules and 6.73×10^{-24} Joules. The nature of variation of J values in these two cases is shown in figures 1 and 2.

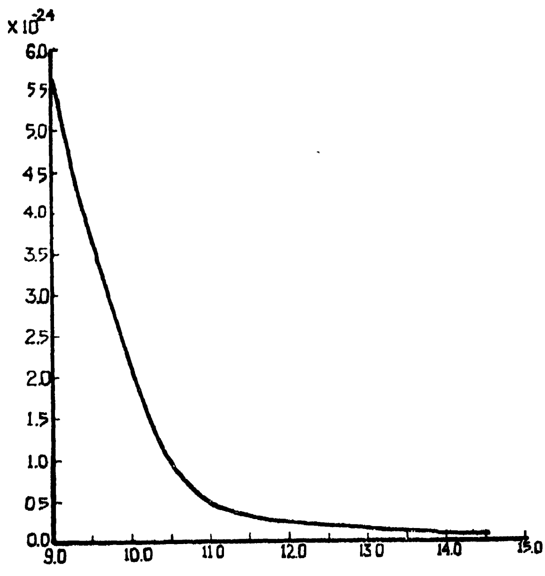

Fig. 1. Variation of exchange integral J with concentration in DPPH.
x axis. Mean spin distance in Angstroms.
y axis. Exchange Integral J in Joules.

DISCUSSION

The first graph indicates that the variation of exchange integral J between mean spin distances of 11.5Å and 14.5Å is very slow but it starts increasing very rapidly as the mean spin distance is decreased below it. This shows that the nature of exchange interaction below 11.5Å is different than above it. This kind of behaviour of exchange interaction may be probably due to the contribution of some short range effect when the spins come closer together.

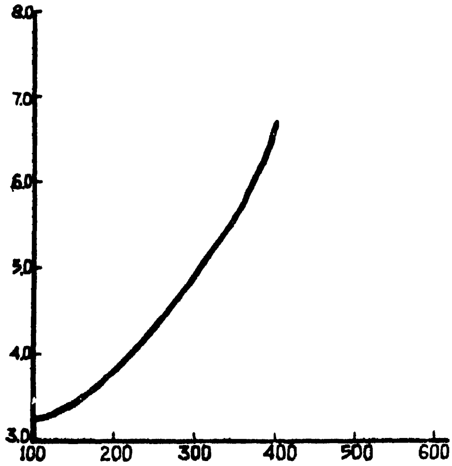

Fig. 2. "Variation of exchange integral J with temperature in Power DPPH."
x axis. Temperature in °K.
y axis. Exchange integral J in Joules.

The graph 2 which represents the variation of J with temperaure shows that the value of J increases as the temperature rises. Walter etal. (1956) have found that it is not only the exchange interaction but there are other factors also which are responsible for the narrowing. They have discussed the motional narrowing due to the delocalization of the unpaired electrons in molecular orbitals. In free radicals the electrons will pass over several atoms in its orbitals and this motion at higher temperature may produce more averaging of the dipole dipole interaction and thus causing the narrowing of the lines. One may therefore say that at higher temperatures the more narrowing is due to the combined effect of exchange interaction and motional narrowing.

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